On the transient Fluctuation Dissipation Theorem after a quench at a critical point

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Abstract. - The Modified Fluctuation Dissipation Theorem (MFDT) proposed by G. Verley et al. *(EPL 93, 10002, (2011))* for non equilibrium transient states is experimentally studied. We apply MFDT to the transient relaxation dynamics of the director of a liquid crystal after a quench close to the critical point of the Fréedericksz transition (Ftr), which has several properties of a second order phase transition driven by an electric field. Although the standard Fluctuation Dissipation Theorem (FDT) is not satisfied, because the system is strongly out of equilibrium, the MFDT is perfectly verified during the transient in a system which is only partially described by Landau-Ginzburg (LG) equation, to which our observation are compared. The results can be useful in the study of material aging.

After a sudden change of a thermodynamic parameter, such as temperature, volume and pressure, several systems and materials may present an extremely slow relaxation towards equilibrium. During this slow relaxation, usually called aging, these systems remain out-of equilibrium for a very long time, their properties are slowly evolving and equilibrium relations are not necessarily satisfied during aging. Typical and widely studied examples of this phenomenon are glasses and colloids where many questions on their relaxation dynamics still remain open [1,2]. Thus in order to understand the minimal ingredients for aging, slow relaxations have been studied theoretically in second order phase transitions when the system is rapidly quenched from an initial value of the control parameter to the critical point [3–6]. Because of the critical slowing down and the divergency of the correlation length the relaxation dynamics of the critical model shares several features of the aging of more complex materials. One of the questions analyzed in this models is the validity of the Fluctuation Dissipation Theorem (FDT) during the out of equilibrium relaxation [8–11]. In equilibrium, FDT imposes a relationship between the response of the system to a small external perturbation and the correlation of the spontaneous thermal fluctuations. When the system is out of equilibrium FDT does not necessarily hold and it has been generalized as

$$k_B T \; X(t,t_w) \; \chi(t,t_w) \quad = \quad C(t,t) - C(t,t_w) \qquad (1)$$

where k_B is the Boltzmann constant, T the bath temperature, $C(t,t_w) =< O(t)O(t_w) > - < O(t) >< O(t_w) >$ ($< . >$ stands for ensemble-average) the correlation function of the observable $O(t)$. The function $\chi(t,t_w)$ is the response to a small step perturbation, of the conjugated variable h of O, applied at time $t_w < t$:

$$\chi(t,t_w) = \frac{< O(t) >_h - < O(t) >_0}{h}|_{h\to 0} \qquad (2)$$

where $< O(t) >_h$ and $< O(t) >_o$ denote respectively the mean perturbed and unperturbed time evolution. The function $X(t,t_w)$ is equal 1 in equilibrium whereas in out-equilibrium it measures the amount of the FDT violation and it has been used in some cases to define an effective temperature $T_{eff}(t,t_w) = X(t,t_w)T$.

The above mentioned models of the quench at critical points allows a precise analysis of the pertinence of this definition of T_{eff} [8]. In spite of the theoretical interest of these models only one experiment has been performed on the slow relaxation dynamics after a quench at the critical point [7]. The role of this letter is to experimentally analyze the theoretically predictions in a real system affected by finite size effects and unavoidable imperfections. We

also analyze another important aspects of the FDT in out of equilibrium systems. Indeed several generalizations of FDT has been proposed [9–17] but almost all of them can be applied to non-equilibrium steady states [18, 19] and are not useful for the transient time evolution which follows the quench at the critical point. As far as we know there are only two formulations of FDT [20,21], which are useful for these transient states and the second purpose of this letter is to discuss the application of the Modified FDT (MFDT) of ref. [20].

Before describing the experimental set-up we summarize briefly the formulation of the MFDT of ref. [20] . Let us consider the relaxation dynamics of a system, which has been submitted at time $t = 0$ to a sudden change of its control parameters. At time t after the quench, this relaxation is characterized by the variable $x(t)$, by the observable $O(x(t))$ and by the probability density function $\pi(x(t), h(t))$. Here $h(t)$ is an external control parameter which is used to perturb the dynamics. We define a pseudopotential $\Psi(t, h) = -\ln[\pi(x(t), h)]$ and an observable $B(t) = -\partial_h \psi(t, h)|_{h\to 0}$, with $h \neq 0$ constant for $t > 0$ and $h = 0$ for $t < 0$. The MFDT reads:

$$\chi(t, t_w) \quad = \quad < B(t)O(t) > - < B(t_w)O(t) > \qquad (3)$$

Eq.3 defines the response function $\chi(t, t_w)$ of $O(t)$ to a step perturbation of h applied at t_w, with $0 < t_w < t$. Notice that in this case h can be any parameter of the system and it does not need to be the conjugated variable of $O(t)$. In this letter we will analyze how MFDT (eq.3) can be applied to the experimental data using the quench at the critical point in a non ideal system.

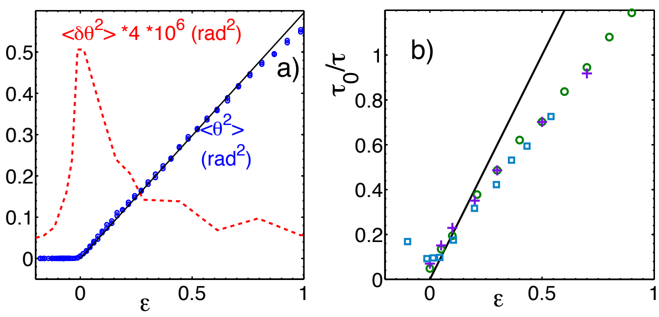

Fig. 1: Phase diagram of the Freedericksz Transition in 5CB. a) Dependence on ϵ of $\theta_o^2 =< \theta >^2$ (blue dots) and of the variance (dashed red line) of θ multiplied by 4 10^6 to be on the same scale. The solution of the LG equation ($\mu = 0$) is the straight black line. b) τ_o/τ is plotted as a function of ϵ. The prediction of LG ($\mu = 0$) is the black straight line. The measured relaxation time deviates significantly from the predicted one even for values of ϵ where the stationary solution of LG, plotted in a) seems to reproduce the data.

The experimental system where we study these properties and the MFDT is the Freedericksz Transition (FrTr) in a nematic liquid crystal (LC) submitted to an external electric field $\vec{E}$. Specificly in our experiment we use the 5CB (p-pentyl-cyanobiphenyl, 5CB, produced by Merck). The experimental apparatus has been already described [22, 23] and we summarize here only the main features. The LC is confined between two glass plates, separated by a distance L =13.5 μm. The surfaces in contact with LC molecules are coated by ITO to apply an electrical field. Then, a polymer layer (rubbed PVA) is deposited to insure a strong anchoring of the 5CB molecules in a direction parallel to the plates. In the absence of any external field, the molecules in the cell align parallel to those anchored at the surfaces. Applying a voltage difference U between the electrodes, the liquid crystal is submitted to an electrical field perpendicular to the plates. To avoid polarization, the applied voltage is modulated at a frequency f = 10 kHz $\left[U = \sqrt{2}U_0 \cos(2\pi f t)\right]$. When U_0 exceeds a threshold value U_c, the planar states becomes unstable and the molecules rotate to align with the electrical field. To quantify the transition we measure the spatially averaged alignment of the molecules determined by the angle θ between the molecule director and the surface. Such measurement relies upon the anisotropic properties of the nematic. This optical anisotropy can be precisely measured using a very sensitive polarization interferometer [22] which gives a signal $\varphi \propto \theta^2$. At $U \simeq U_c$ the dynamics is usually described by a Landau-Ginzburg (LG) equation although as pointed out in ref. [23] this is a very crude approximation, which has several drawbacks. In a very first approximation the dynamics of the mean relaxation $\theta_0(t) = \langle\theta(t)\rangle$ is ruled by the following Ginzburg-Landau equation :

$$\tau_0 \dot{\theta}_0 = \epsilon\theta_0 - \frac{\alpha}{2}\left(\theta_0^3 - \mu^3\right) \qquad (4)$$

where $\epsilon = (U^2 - U_c^2)/U_c^2$ is the reduced control parameter, the τ_o is a characteristic time of the LC and α a parameter which depends on the elastic and electric anisotropy of the LC. For 5CB $\alpha = 3.36$ and $\tau_o = 2.4s$ for the cell thickness $L = 13.5\mu m$. The residual angle $\mu \simeq 0.1$ at $\epsilon = 0$ comes from cell assembling and preparation and has been discussed in ref. [23]. Furthermore τ_o is not strictly constant but it slightly depends on θ_o^2. The dimensional equation for the fluctuations $\delta\theta(t) = \theta(t) - \theta_0(t)$ is

$$\gamma A L \dot{\delta\theta} \quad = \quad K[(\epsilon - \frac{3}{2}\alpha\theta_o^2)\ \delta\theta + \delta\epsilon\ \theta_o] + \eta \qquad (5)$$

$$\text{with} \quad K \quad = \quad \frac{\pi^2 k_1 A}{L} \qquad (6)$$

where A is the laser cross section, k_1 is one of the elastic constant of LC and η is a delta correlated thermal noise such that $< \eta(t)\eta(t') >= k_B T(\gamma A L)\delta(t - t')$. The term with $\delta\epsilon$ takes into account that during the measure of the response we have to perturb the value of ϵ by applying a short pulse of duration τ_p and amplitude $\delta\epsilon$. The two eqs.4,5 describe in principle the dynamics of the mean deflection θ_o and of the fluctuations $\delta\theta$. However there are several discrepancies with the experimental data which are widely discussed in ref. [23]. We summarize here the most important, which are useful for the discussion. The

phase diagram of FrTr in 5CB and the relaxation times are plotted in figs. 1 a),b) respectively. The solution of LG $\theta_o^2 \simeq 2\epsilon/\alpha$ ($\mu = 0$ in eq.4) reproduces the stationary experimental data for $\epsilon \leq 0.6$. Instead the measured relaxation time (fig. 1 b) deviates significantly from the predicted one even for values of ϵ where the stationary solution of LG, (fig. 1 a) seems to reproduce the data. The characteristic time increases but it does not diverge because of $\mu \neq 0$ (see fig.1 and ref. [23]). In fig. 1 a) the variance σ_θ^2 of δ is plotted too. From eq.5 this variance is $\sigma_\theta^2 = k_B T/(K(\epsilon - \frac{3}{2}\alpha\theta_o^2))$ which does not diverge at $\epsilon = 0$ because $\mu \neq 0$.
Thus although eq. 4 and eq.5 are only a rough approximation of the FrTr dynamics, especially at $\epsilon > 0.1$, we use them to fix the framework, and because they are very close to the theoretical mean field approach to the quench at critical point discussed in ref. [6]. Thus it is interesting to check the analogies and differences with respect to the general theory.

The quench is performed by commuting ϵ from an initial value ϵ_i to an $\epsilon_f \simeq 0$ at $t = 0$. As an example we show in fig.2 the time evolution of θ_o for a quench from $\epsilon_i = 0.25$ to $\epsilon_f = 0.01$. The system is relaxing from its initial equilibrium value towards the new one. We describe here the time evolution of the statistical properties and we will discuss at the end the dependence on the initial and final ϵ values. The mean values of the statistical properties are obtained by repeating the quench at least 3000 times.

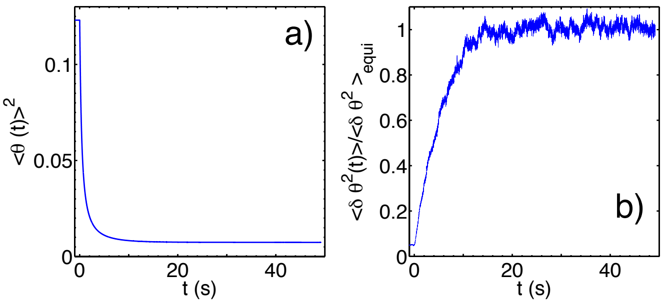

Fig. 2: Quench close to the critical point from $\epsilon_i = 0.25$ to $\epsilon_f = 0.01$. a) Time evolution of the order parameter θ_o^2 before and after the quench preformed at $t = 0$. b) Time evolution of the variance as a function of time. The variance and the mean $\theta^2(t)$ has been obtained by performing 3000 quenches and then making an ensemble average on the quenches at each time.

The time evolutions of $\theta_0^2(t)$ and of the variance $\sigma_\theta^2(t)$ are shown in figs.2a) and b). We see that both quantities relax from the initial to the final equilibrium values ,which are $\theta_e^2 \simeq 2\epsilon/\alpha$ and $\sigma_\theta^2(t) = k_B T/(K(\epsilon - \frac{3}{2}\alpha\theta_e^2))$, where θ_e^2 is the equilibrium value, which is not exactly $2\epsilon/\alpha$ because of the presence of the imperfect bifurcation $\mu \neq 0$ (see fig.1 and ref. [23]). We see that the fluctuation amplitude increases when approaching the critical point.

In Fig.3 we plot $C(t, t_w) =< \delta\theta(t)\delta\theta(t_w) >$ as a function of $t - t_w$ at various t with $t > tw > 0$. We see that $C(t, t_w)$ develops very long decays when t is increased. In order to

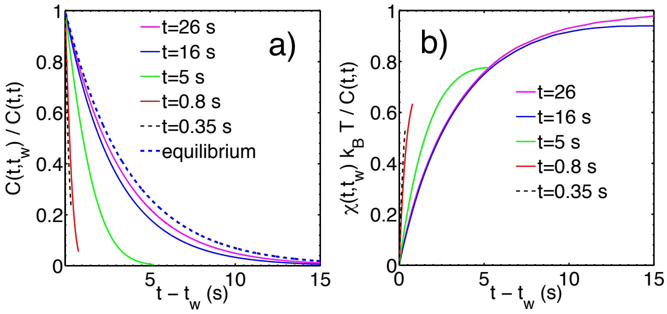

Fig. 3: The correlations functions (a) and the integrated responses (b) (computed at various fixed times t and $0 < t_w < t$ during the relaxation after the quench) are plotted as a function of $t - t_w$.

study FDT we need to measure the response by perturbing the systems with a pulse of amplitude $\delta\epsilon = 0.4$ and $\tau_p = 1ms$ at time t_w. As an example, in fig.4a) we plot the time evolution perturbed at $t_w = 5s$ and in fig.4b) the time evolution of the difference $< \Delta\theta(t) >=< \theta_\delta(t) > -\theta_o(t)$ between the perturbed $\theta_\delta(t)$ and the unperturbed $\theta_o(t)$. As it can be seen in eq.5 the amplitude of the perturbation is $K\delta\epsilon(t_w)\theta(t_w)\tau_p$. Thus the impulse response function is $R(t, t_w) =< \Delta\theta(t) > /(\delta\epsilon(t_w)\theta(t_w)\tau_p)$ for $t_w < t$. We repeat the experiments N_p times by sending at each quench a pulse at a different time $t_{w,i}$ with $[t_{w,1} = 0, ..., t_{w,Np} = 20s]$. Then the integrated response is

$$\chi(t, t_{w,m}) = \sum_{i=m}^{N_t - 1} R(t, t_{w,i+1})(t_{w,(i+1)} - t_{w,i}) \qquad (7)$$

$$\text{such that} \quad t = t_{w,N_t} \text{ and } \chi(t, t) = 0.$$

The measured $\chi(t, t_w)$ is plotted as a function of $t - t_w$ for various t in fig.3.b.

To check the validity of the standard FDT, we plot, in fig.5, $\chi(t, t_w)k_B T/C(t, t)$ as a function of $C(t, t_w)/C(t, t)$ at various fixed t with t_w varying in the interval $0 \leq t_w \leq t$. In this plot FDT is a straight line of slope -1. We see that for t relatively short, compared to τ, the FDT is not satisfied. In fig. 5 we also plot the prediction of ref. [6] for a quench done at $\epsilon = 0$ in a Landau-Ginzburg (LG) equation. We see that for short time the behavior is quite different from that of the LG equation confirming that the dynamics is not very well described by this equation. The behavior at long time is instead related to the fact that the quench is not performed exactly at $\epsilon_f = 0$.

We now apply the MFDT to these data. In order to do that one has to considers that $\delta\theta$ has a Gaussian distribution whose variance is plotted in fig.2. As observable in eq.3 we use $O(x(t)) = x(t) = \delta\theta$. Following the formulation of the MFDT one has to consider the dynamics of $\Psi(t)$ when a small perturbation h is applied at $t = 0$, therefore by the definitions of $\chi(t, t_w)$ (eq.7) and of $O(t)$, we get $< \delta\theta(t) >_h = \chi(t, 0)\ h$ because $< \delta\theta(t) >_0 = 0$. Thus at $h \neq 0$ (switched on at $t = 0$) the probability

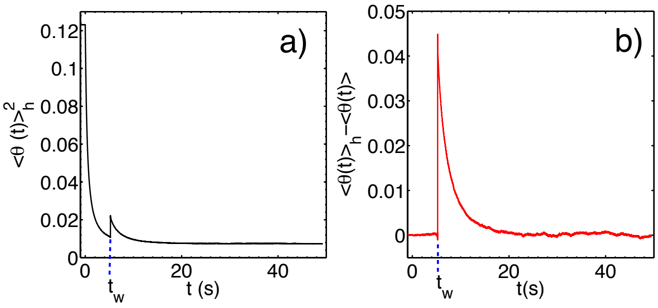

Fig. 4: a) The time evolution has been perturbed at time t_w by a short pulse of amplitude $\delta\epsilon = 0.4$ and duration 1ms. b) The response $\Delta\theta$ to the delta perturbation.

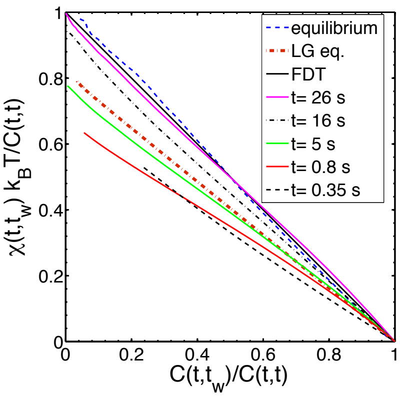

Fig. 5: FDT plot. The function $\chi(t,t_w)k_BT/C(t,t)$ is plotted as a function of $C(t,t_w)/C(t,t)$ at various fixed times t and $0 < t_w < t$ after the quench. In equilibrium this plot is a the straight line of slope -1. We see that at short times t the curves strongly deviate from the equilibrium position. The equilibrium FDT is recovered only for very large t. The red dashed straight line is the prediction [6] for a quench done at $\epsilon = 0$ in a Landau-Ginzburg equation.

density function for of $\delta\theta$ around the mean is

$$\pi(\delta\theta(t), h) = \sqrt{1/(2\pi\sigma^2(t))}\exp(-\frac{(\delta\theta - \chi(0,t)\ h)^2}{(2\sigma_\theta^2(t))}), \quad (8)$$

where we assume that if h is small enough then the dependence of $\sigma_\theta^2(t)$ on h can be neglected. [1]. Therefore from the expression of $\pi(\delta\theta(t), h)$, the definition of $\Psi(\delta\theta(t), h)$ and of $B(t)$ one finds: $B(t) = \delta\theta(t)\chi(t,0)/\sigma_\theta^2(t)$. Thus eq. 3 for this particular choice of variables becomes :

$$\frac{\chi(t,t_w)}{\chi(t,0)} = -\frac{C(t,t_w)\chi(t_w,0)}{\chi(t,0)\sigma_\theta^2(t_w)} + 1 \quad (9)$$

All the quantities in eq.9 have been already measured. Thus in fig.6 we plot $\chi(t,t_w)/\chi(t,0)$, the left term of eq.9, as a function of $C(t,t_w)\chi(t_w,0)/(\chi(t,0)\sigma_\theta^2(t_w))$ for various fixed t and $0 < t_w < t$. We see that all the data points are aligned on a straight line of slope -1 as predicted by eq.9.

[1]This has been verified experimentally and for the dynamic described by eq.6

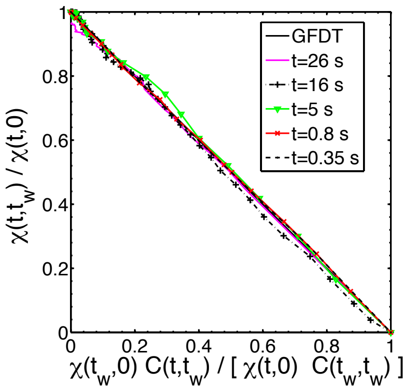

Fig. 6: In order to verify MFDT the left hand side of eq.9, i.e. $\chi(t,t_w)/\chi(t,0)$, is plotted as a function of $C(t,t_w)\chi(t_w,0)/\chi(t,0)\sigma_\theta^2(t_w)$. All the data collapse on the straight line of slope -1 showing that the MFDT prediction for transient is perfectly verified for any t. Notice that the response and the correlations are the same than those used in fig.5, but now they have been normalized as prescribed by the MFDT, i.e. eq.9.

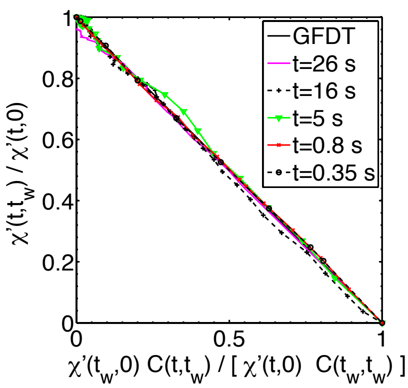

Fig. 7: MFDT recomputed using in eq.9 the $\chi'(t,tw)$ defined in the text. The left hand side of eq..9 is plotted as a function of the right hand side. All the data collapse on the straight line of slope -1 showing that the MFDT prediction for transient is perfectly verified for any t in this case too.

We clearly see that, in contrast to fig.5 where the standard formulation of FDT is recovered only for very large t, MFDT is verified for all times. As pointed out there is no need in MFDT to use for h the conjugated variable of $O(t)$. We can use simply $h = \delta\epsilon$. In such a case we define the response function as $R'(t,t_w) =< \Delta\theta > /(\delta\epsilon\ \tau_p)$ and the $\chi'(t,t_w)$ is obtained by inserting $R'(t,t_w)$ in eq.7. The MFDT computed using in eq.9 $\chi'(t,t_w)$ instead of $\chi(t,t_w)$ is checked in fig.7 where the left hand side of eq.9 is plotted as a function of the right hand side. We see that the MFDT is verified in this case too .

All the data presented in this paper correspond to a quench from $\epsilon_i \simeq 0.25$ to $\epsilon_f \simeq 0.0$, however the main statistical features, here described, are independent on the

starting and final points. The final point influences the duration of the out of equilibrium state, which depends on the distance from the critical point. The small difference with the results in ref. [7] is due to a slightly non linear response in that reference.

As a conclusion in this letter we have applied to a quench a the critical point of Fréedericksz transition (Ftr), the Modified Fluctuation Dissipation Theorem for transient, proposed in ref [20]. We find that although the equilibrium FDT is strongly violated the GFDT is very well satisfied, independently of the chosen response. It is interesting to point out that the result is interesting because although the system presents several differences with respect to the LG equation, it is affected by finite size effects and the quench is not performed exactly at the critical point the dynamics still presents features at the critical quenching.

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